PATENT SPECIFICATION

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(54) LIQUID CRYSTAL DISPLAY DEVICE

(71) We, SHARP KABUSHIKI KAISHA (trading under the name of SHARP CORPORATION), a Japanese Body Corporate, of No. 22—22, Nagaike-cho, Abeno-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a liquid crystal display device. More particularly, it relates to the use in such a display device of a liquid crystal composition having an improved electrically induced turbidity and electro-optic response speed.

A typical liquid crystal electro-optic device consists of two spaced parallel electrode plates having a nematic liquid crystal material therebetween in the form of a normally transparent layer. When a voltage is applied between the electrode plates the layer becomes so turbid that the transmission of light is prevented. By utilization of this effect, various electro-optic apparatus have been manufactured, such as light shutters and display devices.

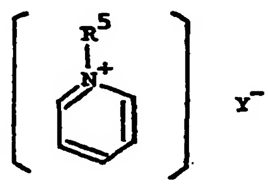
In order to improve the induced turbidity of the electrooptic response speed of the liquid crystal layer it has been proposed to incorporate certain modifiers into the layer. Examples of the modifiers previously used as quaternary ammonium halides, phenols and organic acids. With these conventional modifiers, however, a sufficient and satisfactory improvement could not be achieved.

We have now surprisingly discovered that the incorporation of certain ammonium or pyridinium compounds into a liquid crystal layer can remarkably increase the turbidity and the electro-optic response speed of the liquid crystal layer. It has also been found that such incorporation also assures in an electro-optic device the regular arrangement of the molecules of the liquid crystals material in the liquid crystal layer in the absence of an electric field or current. It has further been found that the degree of orientation of the liquid crystal material in the device is enhanced by the formation of a film of certain inorganic materials on the inner surfaces of the plates serving as the electrodes and accommodating the liquid crystal material between them.

According to the present invention, there is provided a liquid crystal display device which comprises two spaced parallel plates, each provided with an electrode and comprising a film of SiO_x ($0<x\leqslant 2$) or MgF_2, and a liquid crystal layer between the said plates, the layer consisting of a liquid crystal composition which comprises a liquid crystal material and as a modifier at least one ammonium compound of the general formula:

$$\left[R^2-\overset{\displaystyle R^1}{\underset{\displaystyle R^3}{\overset{|}{\underset{|}{N^+}}}}-R^4 \right] X^- \qquad (I)$$

wherein R^1 is an alkyl group or an aralkyl group, R^2, R^3 and R^4 are each an alkyl group and X is an organic acid anion provided that the alkyl group represented by R^2 includes a straight carbon chain with at least 5 carbon atoms more than the total number of carbon atoms in any of the other groups represented by R^1, R^3 and R^4, and/or at least one pyridinium compound of the general formula:



(II)

wherein R^5 is an alkyl group including a straight carbon chain with at least 6 carbon atoms, Y is an organic acid anion and the pyridine ring may optionally bear one or more aromatic ring system condensed thereon.

The alkyl groups R^1, R^3 and R^4 usually contain from 1 to 10 carbon atoms, preferably from 1 to 5 carbon atoms. Examples of such alkyl group are methyl, ethyl, propyl, isopropyl, and butyl. The aralkyl group R^1 usually contains from 7 to 12 carbon atoms, preferably from 7 to 10 carbon atoms. Examples of such aralkyl groups are benzyl and phenethyl.

The alkyl groups R^2 and R^5 usually contain from 6 to 30 carbon atoms, preferably from 12 to 20 carbon atoms. The alkyl group R^2 includes a straight carbon chain in which the number of carbon atoms is at least 5 and preferably 5 to 20 more than the total number of carbon atoms in any of the alkyl or aralkyl groups R^1, R^3 and R^4.

Since a longer straight carbon chain in the alkyl groups R^2 and R^5 produces a higher turbidity but has a tendency to make the response speed slower, preferably the number of the carbon atoms in these alkyl groups is maintained between about 12 and 20 when the resulting liquid crystal composition is intended for use in apparatus demanding a quick response speed such as desk calculators, watches and measurement devices. In this case, the alkyl groups R^1, R^3 and R^4 and the aralkyl group R^1 preferably have 1 to 5 carbon atoms and 7 to 10 carbon atoms, respectively.

The pyridine ring in the pyridinium compound may optionally bear one or more aromatic ring systems condensed thereon. The aromatic ring system may be monocyclic or polycyclic and also carbocyclic (e.g. a benzene ring or naphthalene ring system) or heterocyclic such as nitrogen-containing heterocyclic (e.g. pyridine ring or quinoline ring system). Preferred examples of the pyridine or condensed pyridine are pyridine, quinoline or isoquinoline.

The preferred ammonium and pyridinium compounds are those of formula (I) wherein R^1 is a methyl, ethyl or benzyl group, R^2 is a C_{12}—C_{20} alkyl group (particularly dodecyl or cetyl), R^3 is a methyl group and R^4 is a methyl group and those of formula (II) wherein R^5 is a C_8—C_{20} alkyl group (particularly dodecyl or cetyl).

The anion X^- or Y^- is an organic acid anion. Examples of the organic acid are carboxylic acids and sulfonic acids. Particularly preferred is the residue of a monocarboxylic acid such as benzoic acid optionally having an electron attracting group on the benzene ring (e.g. benzoic acid, cyanobenzoic acid, dinitrobenzoic acid and isopropylbenzoic acid).

The liquid crystal material may be any conventional liquid crystal material of negative dielectric anisotropy such as Schiff bases, azoxy compounds and esters. Examples of preferred liquid crystal materials are *p*-methoxybenzylidene-*p'*-*n*-butylaniline, *p*-ethoxybenzylidene-*p'*-*n*-butylaniline, *p*-butoxybenzylidene-*p'*-butylaniline, *p*-methoxybenzylidene-*p'*-hexylaniline, *p*-ethoxybenzylidene-*p'*-hexylaniline, *p*-methoxy-*p'*-ethylazoxybenzene, *p*-methoxy-*p'*-butylazoxybenzene, *p*-methoxy-*p'*-pentylphenyl benzoate and *p*-hexyloxy-*p'*-pentylphenyl benzoate. These materials may be used alone or in combination.

The amount of the ammonium or pyridinium compound to be incorporated into the liquid crystal material is generally from 0.01 to 1.00% by weight, preferably from 0.03 to 0.50% by weight based on the weight of the liquid crystal material. The incorporation may be effected in conventional manner.

As stated above, the liquid crystal composition used in this invention has an

improved turbidity and response speed. Simultaneously, in an electro-optic device the liquid crystal composition has an enhanced degree of orientation of the molecules of the liquid crystal material in the absence of an electric field or current. This is advantageous, since the enhancement of the orientation which is necessary to increase the contrast between the light scattering portion and the non-light scattering portion was previously achieved by incorporating a particular orientating agent into the liquid crystal material or applying such an orientating agent onto the surface of the plate to be used as the electrode.

While the liquid crystal composition used in the invention has *per se* a very satisfactory degree of orientation, when used in an electro-optic device, its orientation may be further enhanced by forming a coating film of SiO_x ($0<x\leq 2$) and/or MgF_2 on the surface of a plate to be used as an electrode which contacts the liquid crystal composition in use. The thickness of such film is usually not more than 1000Å, preferably not more than 500Å, and generally from 100 to 200Å. The formation of the film may be effected in conventional manner, such as by spraying or vacuum evaporation. The film also serves to protect the electrode.

The liquid crystal display devices of the present invention may be various electro-optic apparatus, and in particular dynamic scattering type liquid crystal display devices.

The present invention will be further described with reference to the following Examples.

Example 1.

p-Methoxybenzylidene-*p'*-butylaniline and *p*-ethoxybenzylidene-*p'*-butylaniline are mixed together in a proportion of 60:40 by weight to make a liquid crystal composition (A).

The liquid crystal composition (A) is admixed with a conventional modifier (i.e. tetrabutylammonium bromide) to make a liquid crystal composition (B). Separately, the liquid crystal composition (A) is admixed with each of benzyldimethylcetylammonium, dinitrobenzoate, benzyldimethylcetylammonium, nitrobenzoate, benzyldimethylcetylammonium isopropylbenzoate, benzyldimethylcetylammonium benzoate and benzyldimethylcetylammonium trimellitate to make liquid crystal compositions (C), (D), (E), (F) and (G).

Two glass plates, each provided with a thin film of tin oxide as a transparent electrode on the surface, are arranged opposite and parallel in such a manner that the transparent electrodes are positioned inside to make a cell having a distance of about 20 μm between the electrodes. The cell is filled up with the liquid crystal composition as prepared above to make a transparent, thin layer.

An alternating voltage (60 Hz, 25 V) is applied between the electrodes, and the electric current passed through the electrodes, the response speed, and the light transmittance are measured.

The results are shown in Table 1 wherein the orientation of the liquid crystal material is also shown.

Table 1

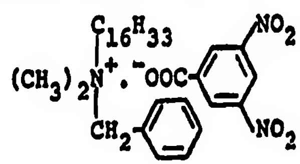
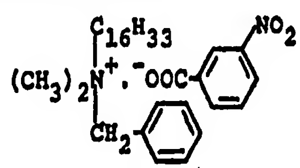
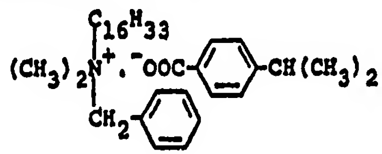
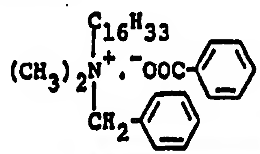
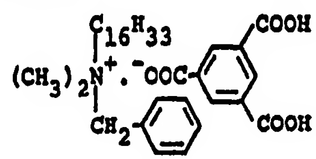
Composition	Modifier	Amount of modifier incorporated (% by weight)	Response speed (msec)		Current ($\mu A/cm^2$)	Transmittance (%)	Orientation
			Rising time	Dropping time			
A	Not used	0	-	-	1	100	None
B	Tetrabutylammonium bromide $(C_4H_9)_4N^+.Br^-$	0.1	70	400	5	30-40	None
C	Benzyldimethylcetylammonium dinitrobenzoate 	0.25	38	208	66.9	20	Vertical orientation
D	Benzyldimethylcetylammonium nitrobenzoate 	0.25	57	330	22	17.5	Vertical orientation

Table 1 (Continued)

Com-position	Modifier	Amount of modifier incorporated (% by weight)	Response speed (msec)		Current ($\mu A/cm^2$)	Trans-mittance (%)	Orientation
			Rising time	Dropping time			
E	Benzyldimethylcetylammonium isopropylbenzoate 	0.25	60	396	16.5	22	Vertical orientation
F	Benzyldimethylcetylammonium benzoate 	0.05	55	270	12	20	Vertical orientation
G	Benzyldimethylcetylammonium trimellitate 	0.05	89	200	2.0	38.7	Horizontal orientation

From the above results, it is understood that the liquid crystal compositions (C), (D), (E) and (F) are much improved in the turbidity and the response speed and affords the regular arrangement of the molecules of the liquid crystal material without any other orientating agent.

Example 2.

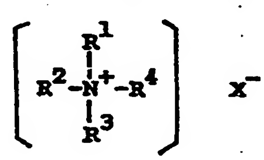
In the accompanying drawing which shows a sectional view of a liquid crystal display device, 1 and 2 indicate glass plates which have electrodes 4 and 5 on their surfaces. On the surfaces of the electrodes 4 and 5, SiO coating films 6 formed by vacuum evaporation are provided. Between the films 6, a liquid crystal composition 3 is arranged so that via the electrodes 4 and 5 a voltage may be applied across the liquid crystal composition. A spacer for setting the distance between the plates 1 and 2 is indicated by 7, and 8 is a sealing material.

The liquid crystal composition 3 consists of a mixture of *p*-methoxybenzylidene-*p'*-*n*-butylaniline and *p*-ethoxybenzylidene-*p'*-*n*-butylaniline in a proportion of 60:40 by weight and incorporates benzyldimethylcetylammonium dinitrobenzoate in an amount of 0.25% by weight on the basis of the combined amount of the said liquid crystal materials.

The liquid crystal display device as constructed above shows a high speed and also has an improved orientation.

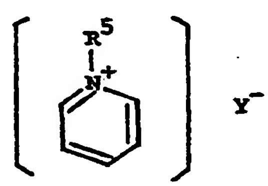
WHAT WE CLAIM IS:—

1. A liquid crystal display device which comprises two spaced parallel plates, each provided with an electrode and comprising a film of SiO_x ($0<x\leqslant2$) or MgF_2, and a liquid crystal layer between the said plates, the layer consisting of a liquid crystal composition which comprises a liquid crystal material and as a modifier at least one ammonium compound of the general formula:



(I)

wherein R^1 is an alkyl group or an aralkyl group, R^2, R^3 and R^4 are each an alkyl group and X is an organic acid anion provided that the alkyl group represented by R^2 includes a straight carbon chain with at least 5 carbon atoms more than the total number of carbon atoms in any of the other groups represented by R^1, R^3 and R^4, and/or at least one pyridinium compound of the general formula:



(II)

wherein R^5 is an alkyl group including a straight carbon chain with at least 6 carbon atoms, Y is an organic acid anion and the pyridine ring may optionally bear one or more aromatic ring systems condensed thereon.

2. A liquid crystal display device as claimed in claim 1 wherein the modifier is an ammonium compound of formula (I) wherein R^1 is an alkyl group having 1 to 5 carbon atoms or an aralkyl group having 7 to 10 carbon atoms, R^2 is an alkyl group having 12 to 20 carbon atoms, R^3 and R^4 are each an alkyl group having 1 to 5 carbon atoms and X is an organic monocarboxylic anion.

3. A liquid crystal display device as claimed in claim 2 wherein R^1 is a methyl, ethyl or benzyl group, R^2 is a C_8—C_{20} alkyl group, R^3 and R^4 are each a methyl group and X is the anion of a substituted or unsubstituted benzoic acid.

4. A liquid crystal display device as claimed in claim 1 wherein the modifier is a pyridinium compound of formula (II) wherein R^5 is an alkyl group having 12 to 20 carbon atoms, Y is the anion of an organic monocarboxylic acid and the pyridine ring is optionally condensed with a single carbocyclic or nitrogen-containing heterocyclic ring.

5. A liquid crystal display device as claimed in claim 4 wherein R^5 is a C_{12}—C_{20} alkyl group, Y is the anion of a substituted or unsubstituted benzoic acid and the pyridine ring is optionally condensed with one benzene ring.

6. A liquid crystal display device as claimed in any one of the preceding claims wherein the liquid crystal material is *p*-methoxybenzylidene-*p'*-*n*-butylaniline or *p*-ethoxybenzylidene-*p'*-*n*-butylaniline.

7. A liquid crystal display device as claimed in any one of the preceding claims wherein the modifier is incorporated into the liquid crystal material in an amount of from 0.01 to 1% by weight based on the weight of the liquid crystal material.

8. A liquid crystal display device as claimed in claim 7 wherein the modifier is incorporated into the liquid crystal material in an amount of from 0.03 to 0.5% by weight based on the weight of the liquid crystal material.

9. A liquid crystal display device as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

10. A liquid crystal display device as claimed in claim 1 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.

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1523808 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale